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ENHANCED GLOW DISCHARGE PRODUCTION OF OXYGEN

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Final Report
For the period ending December 31, 1997

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Background

Studies starting in late seventies have shown Mars atmosphere can be used as a feedstock for oxygen production using simple chemical processing systems during early phases of the Mars exploration program. This approach has been recognized as one of the most important in-situ resource utilization (ISRU) concepts for enabling future round trip Mars missions.

It was determined a decade ago that separation of oxygen can be accomplished efficiently by permeation through a silver membrane at temperatures well below 1000 K . This process involves adsorption of atomic oxygen on the surface and its subsequent diffusion through a silver lattice via an oxygen concentration gradient. We have determined recently that glow discharge can be used to liberate atomic oxygen from Mars atmosphere and that the oxygen can be collected through a silver permeation membrane . Recently, we demonstrated a substantial increase in energy efficiency of the process by applying a radio frequency discharge in combination with a silver permeation membrane . The experiments were performed using pure carbon dioxide in the pressure range equal to Mars surface conditions. Energy efficiency was defined as the ratio of the energy required to dissociate a unit mass of oxygen from carbon dioxide to the (electrical) energy consumed by the overall system during the dissociation and collection process.

The research effort, started at NASA Langley Research Center, continued with this project. Oxygen production apparatus, built and operated under the research grant NAG1-1140 was relocated to the Atomic Beams Laboratory at ODU in July 1996, being since then in full operation.

RF Characterization/Optimization Research

The results of computer modeling show that the chemical composition of Martian atmospheric gas is changed substantially in the radiofrequency discharge. The gas mixture containing predominantly carbon dioxide is transformed into the mixture containing large proportions of atomic and molecular oxygen, carbon monoxide, and smaller amounts of carbon dioxide and other gases. The residual gas, after partial separation of oxygen, has a potential for further utilization, which is the subject of our current investigation.

Laboratory tests on the "Martial air" gas mixture (95.66% CO_2, 2.75% N_2, 1.59% Ar) to simulate more realistic conditions for oxygen production from the Mars atmosphere, are completed. Silver membrane acted as one of the electrodes in the capacitively-coupled radio-frequency (RF-CCP) discharge. The oxygen flux was of input RF power density (0.3 to 2.2 W/cm^2), silver permeation membrane temperature (670 K to 780 K), Martial air pressure (4 to 8 Torr), interelectrode distance (3 to 6 mm) and RF operating frequency (20 to 40 MHz). The efficiency of oxygen separation is being tested as a function of the thickness of the silver membrane and the operating temperature. They have shown no substantial change in oxygen flux with respect to the radiofrequency discharge in pure carbon dioxide. After successful introduction, the Martian air mixture is currently being routinely used in the RF-CCP discharge.

An impedance-matching circuit was introduced to reduce RF power loss on reflection. Presently the discharge input power is about 80% of total forward RF power. We expect with the optimal design to reduce the loss below 10%.

Ultrathin Membrane Studies

Several alternative approaches are being discussed for the reduction of the thickness of the silver permeation membrane.

Two complementary approaches to obtain high oxygen yield are currently being developed. One of them, the thin silver sheet assembly containing the self-supporting membrane with the thickness in the order of 0.1 mm is currently tested. Design of the membrane assembly with thin silver sheets on perforated support is under development. The thickness of these membranes are less than 100 μm. Several materials were considered as the candidates for perforated support of thin silver membranes. Material of choice is presently the perforated silver plate. According to a standard vacuum design formula, dimensions of holes in the perforated silver plates should not present a technical problem even for the lowest, submicron membrane thickness. It is expected that the second approach achieve oxygen extraction level close to the theoretical limit. Tests of the durability of the membranes at high temperatures in the presence of the radiofrequency discharge and the structural properties of membrane assemblies constitute the important part of present development activity.

Estimates of Scaled-up Units

Based on the present state of our knowledge on oxygen production in a RF-CCP discharge and its extraction with silver membrane the minimum surface for 1 kg/day production will be about 0.8 m^2. Total mass of the system including silver, supporting material, heaters, and power supplies is estimated to about 12.5 kg without compressor. This area will be about 8 m^2 for the production level of 10 kg/day. Mass of silver in this case is estimated at 77 kg not including the compressor.

Estimates of Power Requirements

Simple heat-of-reaction considerations give the necessary energy for carbon dioxide decomposition to be 532.1 kJ/mole. Part of the energy, 249.1 kJ/mole, is recovered after recombination of oxygen. The difference is the theoretical minimum energy required for this process. Expressed in terms of energy per unit mass, it is equal to 17.686 MJ/kg. For typical values of RF power currently obtained in our laboratory, $P_{RF} = 0.1\ W/cm^2$, and for the target value of oxygen flux, $J = 5\times10^{16}\ cm^{-2}s^{-1}$, the energy per unit mass required by the RF-CCP discharge combined with silver membrane permeation, is 72.7 MJ/kg. Hence, the estimated efficiency of the process is close to 25%. Further increase of efficiency will be based on the achievement of submicron thickness of silver membrane, increase of oxygen diffusivity, and operation at higher pressures.

Assessment of Technical Readiness

Preliminary design of the radiofrequency cell to be used in the demonstration of oxygen production, was made. The cell will be capable of processing a larger volume of Martian atmospheric gas. It will constitute of a double array of 12 circular silver membranes realized in the self supported membrane technology. The membrane arrays will be implemented in the cell as one of the planar electrodes of the capacitively-coupled RF discharge, parallel to the gas flow. Oxygen will diffuse through silver in perpendicular direction of the gas flow into an evacuated, closed chamber with the volume of about 10 cm^3. The yield of oxygen will be obtained by measuring the pressure and the temperature in the chamber. The laboratory prototype RF-CCP cell will be used for the proof-of-principle tests. The membrane thickness and assembly will be chosen during the next research period to demonstrate maximum reliability and performance.

Research Spin-off

In order to adjust to the time scale of the other ISPP projects and fully compete for participation in Mars Sample Return and Mars Human Exploration as an enabling technology, present research effort has been spinned off in several different ways.

First, a proposal was submitted to NASA Johnson Space Center to develop a proof-of-principle laboratory prototype of RF-CCP reaction cell combined with the silver membrane to extract oxygen from Martian atmospheric gas. The cell will be tested in summer 1998 at MIST Testbed at NASA Johnson Space Center.

Second, a hybrid system including an inductively-coupled plasma RF discharge (RF-ICP) cell and ceramic honeycomb structure developed at Ceramphysics Inc. for oxygen separation is being proposed for development. We are motivated by the finding that the dissociation of carbon dioxide can be increased to almost 100% by a careful design of RF discharge parameters. In the case of total dissociation, the volume separation of oxygen from the reacted gas mixture can be more effective than the surface extraction through silver membrane. One of possible approaches is to dissociate carbon dioxide in a RF discharge and separate oxygen from the reacted gas mixture using a bismuth oxide honeycomb structure. We are presently working out the details of an experiment to demonstrate feasibility of this approach. Other approaches are being considered as well. In the case that a hybrid solution for oxygen extraction proves to be effective, the volume separation will improve substantially the applicability of an RF discharge for oxygen production by dissociation of carbon dioxide.

Third, in order to take fully into account all aspects of Martian atmospheric conditions, a part of our effort is focused on the long-term effects of Martian dust on the system. The property of radiofrequency discharge to trap and enable natural removal of dust particles is being elaborated. It was found that the trapping of particles is size selective. Particles with the smallest size tend to concentrate around the discharge axis, and the largest particles concentrate close to the discharge sheath. Silver membrane, which acts also as one of the electrodes of the discharge is repellent for the dust particles, which are electrically charged in the discharge. The process is therefore naturally protected from contamination by dust particles.

Personnel Changes

During 1997, this project was conducted by Dr. Leposava Vuskovic, together with Dr. Robert L. Ash. Dr. S. Popovic, plasma physicist, joined the team in December of 1996. Dr. Shi left ODU by the end of December, 1996. Dr. Ann Van Orden, material scientist also joined the research team in 1997. The input of John Gleasson from NASA Langley Research Center is appreciated. Thao Dinh, graduate student, is fully engaged in data acquisition.

Publications and Presentations

1. "An Investigation of Radio Frequency Enhanced Glow Discharge Production of Oxygen from Carbon Dioxide" by Z. Shi, D. Wu, and R. L. Ash, 26th International Conference on Environmental Systems, Monterey, CA, *SAE Paper 961598* (1996).

2. "Radio-Frequency-Based Glow-Discharge Extraction of Oxygen from Martian Atmosphere: Experimental Results and System Validation Strategies" by L.Vušković, Z. Shi, R. L. Ash, S. Popovic, and T. Dinh, presented at *First In Situ Resource Utilization (ISRU I) Technical Interchange Meeting* held at Lunar and Planetary Institute, Houston, TX, February 4-5, 1997.

3. "Radio-Frequency Discharge Reaction Cell for Oxygen Extraction from Martian Atmosphere" by L.Vušković, R. L. Ash, S. Popovic, T. Dinh, and A. VanOrden, 27th International Conference on Environmental Systems, Monterey, CA, *SAE Paper 972499* (1997).

4. "Oxygen Production and Separation from Martian Atmosphere by the Radio-Frequency Discharge" by L.Vušković, R. L. Ash, S. Popovic, T. Dinh, and A. VanOrden, presented at *Second In Situ Resource Utilization (ISRU II) Technical Interchange Meeting* held at Lunar and Planetary Institute, Houston, TX, February 4-5, 1997.